

Hydrogenolysis of Carboxylic Acids With Rhodium Oxide

Hydrogenolysis of a carboxylic acid or ester to the corresponding alcohol is one of the more difficult catalytic reductions. Copper chromite catalysts are relatively cheap and are commonly used, but have the disadvantage that reduction may require high temperature (6) or a large amount of catalyst (1). Carboxyl reduction is possible at lower temperatures (150 C) with ruthenium (4) or rhenium (3) oxide catalysts.

Rhodium catalysts have received very little attention for the hydrogenolysis of carboxylic acids.

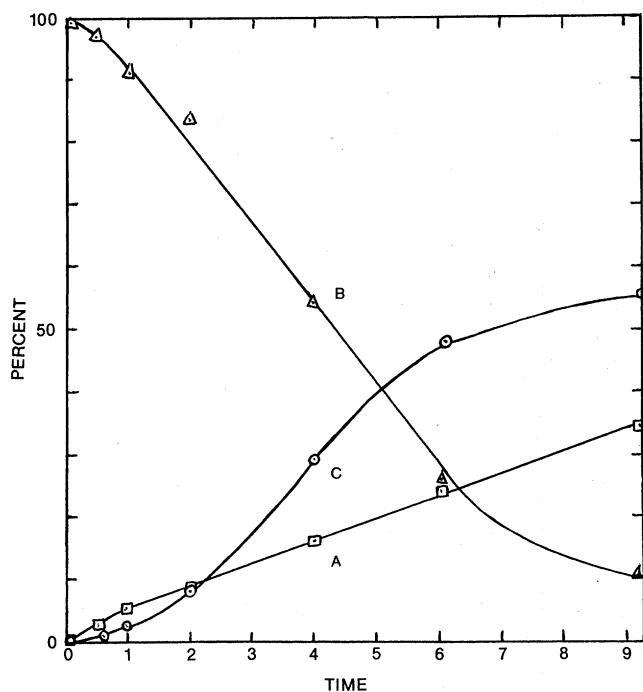


FIG. 1. Distribution of reduction products as a function of time. A, Nonanol; B, Nonanoic acid; C, Nonyl nonanoate.

groups but is said to be a poor catalyst, although no details are given (7). We have recently observed that rhodium oxide can catalyze the reduction of stearic acid to a significant degree (5) and we have now briefly explored the scope of the reaction.

As shown by Table I and Figure 1 carboxylic acids are reduced by rhodium oxide to the corresponding alcohol, then further condensed to the ester. After hydrolysis of the ester the total yield of nonyl alcohol is 49% in 6 hr, 63% in 9 hr. Esters are inert under the reaction conditions (Experiment 6) and hydrogenolysis is slower in non-polar solvents (Experiment 5).

In the reduction of benzoic acid a rapid pressure drop occurs around 75 C, corresponding to saturation of the benzene ring (2). Thus the species undergoing hydrogenolysis is really cyclohexanecarboxylic acid.

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REFERENCES

1. Augustine, R. L., "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, 1965, p. 89.
2. Augustine, R. L., *Ibid.*, p. 74.
3. Broadbent, H. S., G. O. Campbell, W. J. Bartley and J. H. Johnson, *J. Org. Chem.* 24, 1847-1854 (1959).
4. Cornahan, J. E., T. A. Ford, W. F. Gresham, W. E. Grigsby and G. F. Hager, *J. Am. Chem. Soc.* 77, 3766-3768 (1955).
5. Grimm, R. A., J. E. Menting, A. J. Stirton and J. K. Weil, in press.
6. Markley, K., "Fatty Acids," 2nd edition, Vol. 2, Interscience Publishers, New York, 1961, p. 1271-1275.
7. Rylander, P. N., "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, 1967, p. 230.

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TABLE 1
Carboxyl Reductions With Rhodium Oxide
(Charge: Substrate 15 g, solvent 80 ml, Rh₂O₃·5H₂O 0.2 g. Hydrogen pressure 2000 psig.)

Experiment	Substrate	Solvent	Temperature, C	Time, hr.	Products, %	
1	Nonanoic acid	Water	150	6	Nonyl alcohol	25%
					Nonyl nonanoate	48%
					Nonanoic acid	26%
2	Dodecanoic acid	Water	150	6	Dodecyl alcohol	26%
					Dodecyl dodecanoate	37%
					Dodecanoic acid	53%
3*	Octadecanoic acid	Water	175	5	Octadecanol	10%
					Octadecyl octadecanoate	36%
					Octadecanoic acid	40%
4	Benzoic acid	Water	150	6.5	Cyclohexylmethanol	33%
					Cyclohexylmethyl cyclohexanecarboxylate	34%
					Cyclohexanecarboxylic acid	33%
5	Benzoic acid	Cyclohexane	150	3.5	Cyclohexylmethyl cyclohexanecarboxylate	15%
					Cyclohexanecarboxylic acid	85%
6	Methyl nonanoate	Methanol	150	5	No reaction	

* Catalyst 0.1 g; hydrogen pressure 3800 psig.